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Feasibility Study on the Development of Tough, Moisture-Resistant Laminating Resins

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SUMMARY

Wider use of composite materials in commercial aircraft applications is somewhat limited by the sensitivity of current high performance epoxy matrix resins to relatively small amounts of sorbed atmospheric moisture. The elevated temperature, matrix-dominated mechanical properties are significantly reduced in the "wet" condition.

The objective of the program was to demonstrate the feasibility of using cyanate resins as laminating systems with projected cost, handleability, and processing requirements equivalent to 400K (260°F) curing epoxies and to provide laminated structure of equivalent quality but with improved moisture resistance and toughness. Cyanate resins were found to be well suited for these applications. The program preceded from monomer synthesis, through formulation, blending, resin preparation, catalysis studies, prepreg preparation to laminate fabrication and test. The goal of the contract was met with fabrication of a graphite fiber reinforced laminate with 95 percent retention of the original 363K (180°F) flexural strength and 70 percent retention of the 363K (180°F) short beam shear strength after 500 hour exposure to 95+ percent relative humidity at 324K (120°F).

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INTRODUCTION

Elevated temperature property losses in graphite reinforced epoxy resin composites is a chronic problem associated with sorption of atmospheric moisture. The effects are explained as plasticization phenomena brought about by either prolonged exposure to a high humidity environment or cyclic (nonstatic) conditions which include high humidity exposures. The deleterious effects are cumulative as property losses increase until quasi-saturation levels are attained.

A critical requirement for long-term application of any material system is that it should not be severely affected by its use environment. Exposures include conditions expected in the more severe ranges of the use spectrum (high temperature, high loading, etc.) and, of equal importance, those conditions existing in a "passive" environment. The susceptibility of the popular high-performance matrix resins (epoxies) to loss of properties by the apparent plasticizing action of even slight amounts of sorbed atmospheric moisture is well documented. Improved moisture resistance in composites is a definite requirement for expanded use in commercial aircraft applications. Low impact resistance imposes further restrictions on the use of current fiber-reinforced epoxy systems.

Objective

The objective of this program was to demonstrate the potential of cyanate resins as matrices for composites having graphite fiber reinforcements. The overall objective was to develop a laminating resin with cost, handleability, process requirements and mechanical properties equivalent to current high performance 400K (269°F) curing epoxy systems but with improved moisture resistance and toughness.

General Considerations for Resin Characteristics

A semi-empirical approach was used to develop an improved moisture resistant resin system. The "ideal" matrix resin system would have, at a minimum, the following characteristics:

a. Be resinous at room temperature to allow adequate drape and tack characteristics in hot melt coated prepreg form.

b. Cure by an addition or ring opening mechanism with no volatiles evolved during cure.

c. Possess a long shelf life without need of extraordinarily high post-cure temperatures for cure.

d. A glass transition temperature somewhat in excess of the cure temperature, attained by crosslink density and segmental rigidity adjustment.

e. A proper balance of polar/nonpolar structures to ensure adequate cohesive energy density levels but to minimize resin/moisture interaction.

f. Inclusion of bulky, hydrophobic substituents to lower "microvoid" content.

Cyanate Resin Technology

Cyanate resins were chosen for our investigation due to their unique combination of favorable properties. The chemistry from monomer synthesis through polymer formation is straightforward. A cross-linked system is formed through an addition (cyclotrimerization) mechanism. Cured polymer properties are easily modified by choice of appropriately substituted cyanate monofunctional and difunctional monomers. Variations in cross-link density, polarity, cohesive energy density, toughness, hydrophobic character, ultimate glass transition temperature, etc., are readily accomplished by appropriate selection and combination of monomers.

Cyanate resins must be derived from aromatic parent compounds. As seen in Figure 1, a bisphenol is reacted with cyanogen halide to provide a bis cyanate ester which, upon partial thermal reaction, produces a meltable, soluble B-staged resin. Since cure is accomplished at moderate temperatures and without volatile evolution, processing techniques used for epoxy systems are generally applicable. In addition to hot melt prepregging technology, the resin is soluble in several low boiling solvents that can also be employed for impregnation.

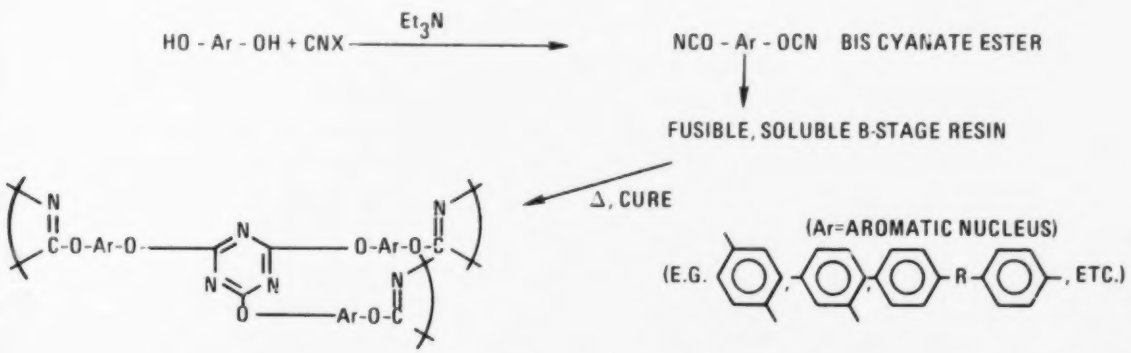


Figure 1. Cyanate Resin Chemistry

Aliphatic substituents can be introduced into the resin only as substituents on the benzene nucleus since aliphatic cyanates are unstable and rearrange to the corresponding isocyanate. Other nonfunctional groups, such as chlorine, bromine, etc., can be introduced into the resin system by appropriate substitution into the aromatic nucleus. Monofunctional cyanates may be added, if desired, to reduce the crosslink density.

TECHNICAL DISCUSSION

Polymer Selection Rationale and Program Outline

The latitude for modification offered in cyanate resin chemistry is quite broad. Briefly, the modifications that would most likely bring about the desired characteristics, would include the following:

a. Non-reactive compatible diluents.

b. Reactive monofunctional diluents.

c. Copolymerization of dissimilar difunctional monomers.

Monofunctional diluents could, in theory, be added at a 50 mole percent level with a difunctional monomer to give a "linear" highly branched polycyanurate molecule. In practice, the unknown reactivities of various monofunctional cyanates, as compared to the reactivity of a single difunctional system, should allow empirical molar substitutions beyond 40 percent. A remote possibility existed that the polymerizing (difunctional) monomer would not react with the monofunctional cyanate. If this occured, the monofunctional cyanate would probably trimerize to a trisubstituted cyanurate and simply behave as a compatible filler in the resin.

Various monofunctional cyanates can be copolymerized with the dicyanates and cured to ascertain their effect upon the moisture response and also to reduce crosslink density. The rationale behind the choice of ring substituents on the monofunctional cyanates depended primarily on three factors: (1) ease of synthesis and stability, (2) the (expected) additive contribution to the "degree of hydrophobicity" of the bulk resin itself, and (3) the anticipated change in microvoid content.

Microvoid content may be most readily visualized as being induced by the internal stresses developed during cure which, because of the highly crosslinked nature of the polytrimerization, are "frozen" into the system. Reduction in crosslink density, such as is obtained by partial replacement of the dicyanate monomer with a monocyanate, would tend to reduce these factors. A further advantage is obtained by various ring substitutions.

The effect of the substituent was expected to manifest itself through two complementary modes: (1) an increase in the "hydrophobic" nature of the system due to a higher hydrocarbon content, and (2) the anticipated effect of "filling" the microvoids with the bulky substituent groups. A loose analogy may be envisioned by referring to "packing efficiency" rationale.

Reduction of overall crosslink density was expected to reduce the "microvoid" content of the resin system. This should be accompanied by a simultaneous decrease in the apparent Tg of the polymer system. The reduced internal strain of the fully cured polymer, brought about by the nominal lowering of crosslink density, was expected to allow a more homogeneous cure to proceed with concurrent "smoothing" of the local variations in microdensity. Accordingly we selected reactive monofunctional cyanates as the most promising route to follow.

The investigation proceeded in the following manner:

a. Add various mole percent loading levels of the substituted monofunctional cyanate to the basic difunctional monomer.

b. Cure the resultant system.

c. Grind a portion of the cured polymer to fine particle size.

d. Expose the powder to 95-98 percent humidity at 324K (120°F) and determine the moisture pickup rate and equilibrium value.

e. Determine Tg (as determined by thermomechanical analysis) on the bulk resin.

f. Screen the various systems for the best and worst examples (both from the standpoint of moisture pickup and Tg effects).

g. Establish bulk resin properties for the best system(s).

h. Evaluate the derived resin(s) as laminate matrices.

Monomer Selection

Previous work (References 1, 2) provided guidelines for selection of difunctional monomer and monofunctional cyanates most likely to suite the goals of the program. The criteria for selection included ease of synthesis and handling, availability, expected physical properties including ultimate Tg, expected contribution to moisture response, anticipated B-stage characteristics, cost and compatibility considerations. Our efforts were restricted to investigation of systems that would undergo

adequate cure after a 400K (260°F) preliminary cure followed by a free-standing 423K (300°F) postcure. A number of potential difunctional dicyanates were considered with our ultimate choices listed below and in Table 1. The selected monofunctional cyanates are also listed in Table 1.

Table 1. Monomer Properties

Cyanate	Melting Point, K (°F) or Boiling Point K (°F) at mm Hg	Literature Melting Point, °F or Boiling Point, °F, at mm Hg	*DSC Trimerization Exotherm, K (°F) Maximum
Monomers			
2,2-Bis(4'-cyanatophenyl) propane (BPADC)	356-357(181-183)	178-180	548(527)
2,2-Bis(4'-cyanatophenyl) hexafluoropropane (BPADC-F)	361-362(190-192)	189-191	488(415)
Monofunctional Diluents			
4-Nonylphenylcyanate (NPC)	404(268) at 0.75 mm	(273-279 at 0.80 mm)	496(433)
4-Phenylphenylcyanate (PPC)	335-336(144-146)	144	490(423)

*The exotherm maximum is defined as the temperature at which the heat of reaction reaches a maximum.

Monomer Synthesis and Preliminary Blend Studies

The two monofunctional and two difunctional cyanate monomers listed in Table 1 were successfully synthesized, following the methods reported by Grigat, et al (Reference 3). The more easily handled (and available) cyanogen bromide was substituted for the more efficient cyanogen chloride in the initial preparations.

This synthesis was used for the small amounts of material needed for preliminary screening and blending studies. The use of the bromide often results in a crude product that is more difficult to purify. Nonetheless, the data obtained from purified material is valid, regardless of reagent chosen. Subsequent preparations used cyanogen chloride gas. Details of these preparations are found in the experimental section.

The trimerization reaction exotherms, determined by DSC measurement, showed the peak temperatures listed in Table 1. The bis-phenol A dicyanate (BPADC) was considerably less reactive than the other monomers. DSC scans of equimolar mixtures of the BPADC combinations with the two monofunctional cyanates showed two exotherm maxima characteristic of each constituent. Combinations of the fluorinated analog, (BPADC-F), with nonylphenylcyanate and 4-phenylphenylcyanate, with more or less equal maxima, conversely showed a single exotherm peak. No significant differences in polymer structure (e.g., nonstatistical distribution of cyanurate substitution) was evident, which could perhaps be expected by these differences in reactivity. However, one apparent difference was uncovered as displayed by the following results obtained with the BPADC/PPC and BPADC-F/PPC systems.

A 50/50 molar mixture of mono- and difunctional monomers would, in principle, yield an essentially linear but highly branched polymer. When equimolar quantities of the dicyanate and monocyanate were coreacted at 477K (400°F) for 16 hours and pulverized to minus 60 mesh particle size, extraction with chloroform showed that the BPADC/PPC system (the greatest difference in exotherm peaks) produced the smallest amount of soluble material (28.1 percent dissolved versus 34.2 percent dissolved for the BPADC-F/PPC system). When the molecular weights of the starting difunctional monomers (288 versus 386) is considered, the difference is even more pronounced. We did not pursue these results since such effort was outside the scope of our program.

Formulation Studies

A natural upper limit on attainable glass transition temperature, Tg, was imposed by the postcure temperature restriction of 423K (300°F). Previous work with cyanate resins had shown a good correlation between cure temperatures and attained Tg. The Tg was generally found to be approximately 20 to 35 degrees above cure temperature after a few hours at that temperature. Hence we felt that systems showing Tg of approximately 444K (340°F) would probably demonstrate "adequate" cure in a few hours at the postcure temperature. Selection of a system capable of much higher Tg (through even higher temperature postcures) was inadvisable since the material would probably not behave predictably. As its high temperature exposure increased, there would be the expected postcure effects that would certainly change the mechanical and physical properties of the resin and composite. Any adverse changes in moisture response would not be desirable, nor would embrittlement or other defects which might become apparent after further cure reaction.

Figure 2 summarizes the glass transition temperatures of the various combinations. All the formulations were given a cure through 16 hours at 477K (400°F) to ensure complete reaction. NPC is more effective than PPC in depressing Tg of both BPADC and BPADC-F throughout the composition range studied.

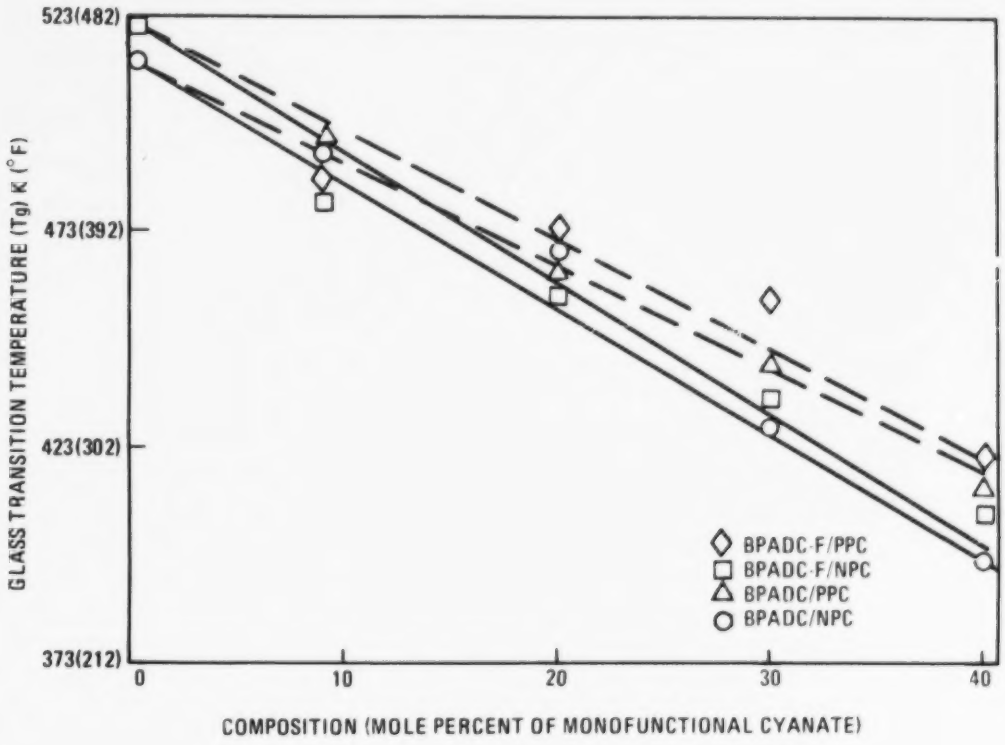


Figure 2. Glass Transition Temperatures of Copolymers

Moisture sorption studies on the polymer mixtures were also investigated. The cured samples were ground to minus 30 mesh particle size and placed in a 98-100 percent relative humidity chamber at 322K (120°F) until constant weight was obtained. Equilibrium was established relatively quickly, usually in three to four days. Additional time caused no weight increases in the samples. The results are summarized in Figure 3, which shows the percent of water absorbed as a function of composition. Generally, ultimate water absorption shows a monotonic decrease as a function of monofunctional cyanate content. All of the samples sorb very small amounts of water (less than 1 percent). As expected, the BPADC-F copolymers sorb less water than the corresponding BPADC copolymers. The BPADC-F/NPC system surprisingly exhibits no water sorption at 30 mole percent NPC. These results reflect a dual effect: 1) the change in polymer makeup, brought about by a reduction in the total polarity

(hydrophilic) content, coupled with an increase in hydrophobic character with the added alkyl or aryl substituents, and 2) the change in polymer structure brought about by the lowering of cross-link density, resulting in an overall reduction of micro-void content.

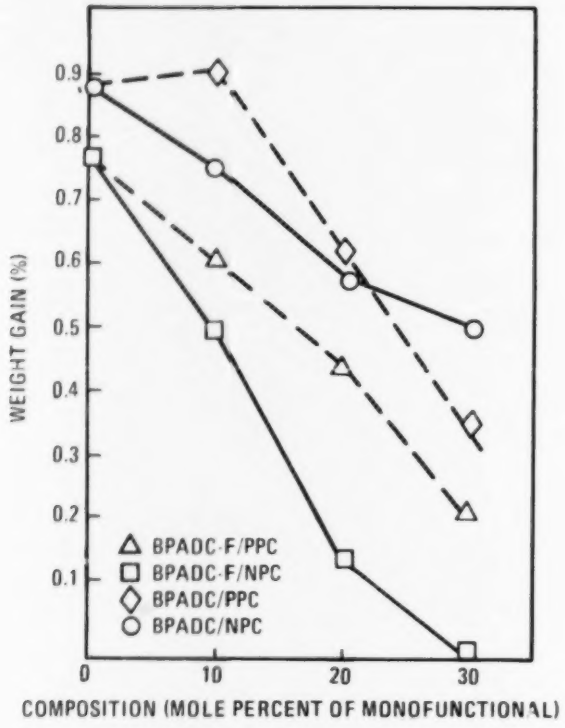


Figure 3. Water Sorption of Copolymers

Specific gravity measurements on the polymerized cyanates as a function of mole percent composition are summarized in Figure 4. On a molar basis, NPC is more effective than PPC in decreasing the specific gravity.

The moisture absorption results were obtained on finely ground samples which absorb and desorb moisture at significantly higher rates than castings due to the very high surface-to-volume ratio. This rapid loss of sorbed moisture upon heating does not allow simple determination of Tg shifts which occur upon moisture uptake.

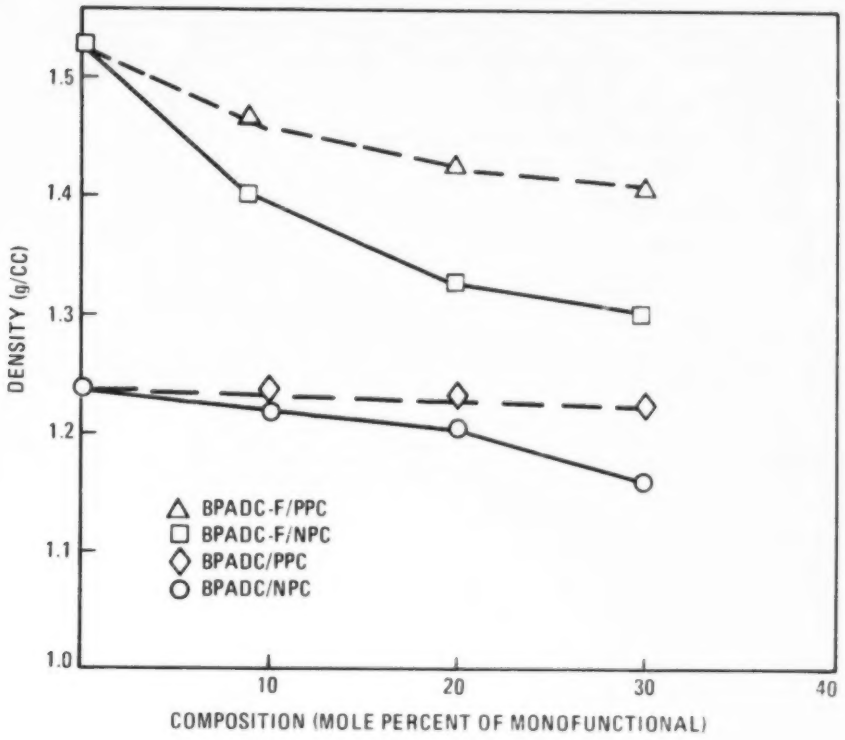


Figure 4. Density of Copolymers

Water boil studies have also been used as a screening technique for moisture studies. Although a direct comparison of the results of the two methods is limited, a 24-hour water boil of selected systems was performed recognizing that these results would represent an extreme in moisture uptake and reflect Tg suppression significantly greater than what would be expected in service environments.

Small discs of the cured polymer measuring approximately 0.35 cm diameter by 0.20 cm thick were boiled 24 hours in distilled water, slowly cooled to room temperature, and soaked in the water for an additional 24 hours. The moisture uptake was measured before and after TMA testing where both expansion techniques and Deflection Temperature Under Load (DTUL) at 3100 KPa (450 psi) compressive load was utilized. The results are presented in Table 2. The onset temperature is reported for both modes along with the extrapolated Tg (by expansion).

To ensure that the moisture sorbed during the water boil was present at reasonable levels during the Tg testing, a rapid rate of heating (50 K/min) was applied. Immediately after the determination of the Tg, the sample was reweighed to determine the amount of residual water in the polymer sample. On the average, the residual moisture was approximately 50 percent of the initial amount. Desorption does indeed

Table 2. Water Boil Test Results

Polymer	Wet Samples*		Dry Samples*			Percent Water Sorbed Before TMA	Percent Water Sorbed After TMA
	Softening Tg (DTUL) K	Extrapolated Tg K	Onset Tg K	Extrapolated Tg K	ΔTg		
BPADC	428	418	473	482	64	2.10	0.80
BPADC + 10% PPC	408	415	469	476	61	1.35	0.85
BPADC + 20% PPC	398	423	463	472	49	1.10	0.55
BPADC + 30% PPC	375	398	436	443	45	1.25	0.44
BPADC + 20% NPC	390	409	440	445	36	1.01	0.62
BPADC-F	428	489	494	503	14	1.00	0.60
BPADC-F + 10% PPC	410	485	460	467	18	1.60	1.00
BPADC-F + 20% PPC	450	471	458	463	8	0.60	0.20
BPADC-F + 30% PPC	450	425	454	458	33	0.50	0.30
BPADC-F + 20% NPC	400	434	453	458	34	0.50	0.24

*Heating Rate 50K/minute

occur rapidly. During the testing of the homopolymers, the discs cracked and shattered due to the rapid evolution of steam in the more brittle matrix. (The homopolymers absorbed almost twice that absorbed by the copolymers.) The copolymers showed no evidence of cracking, an indication of a less brittle matrix.

The glass transition temperatures of the polymers and copolymers are depressed due to the sorption of water. The precise value of the Tg (wet) was difficult to ascertain. Three values are listed in Table 2 corresponding to the three methods used. The softening point is the onset temperature for the DTUL determination. The onset Tg is the onset point during the expansion run (2g load). The extrapolated Tg is the point of intersection of the two slope lines of the expansion run (2g). Precise values were difficult to establish in some cases because the dynamic loss of sorbed water leads to nonlinear behavior.

In several examples, the softening Tg (DTUL) onset was lower than the onset Tg. This is probably due to a plasticization effect of the water which becomes more pronounced under a high load. The higher the water sorption the greater the difference between the extrapolated wet Tg and the Tg observed under dry conditions. An interaction between reduction in microvoid content (bulky pendant groups), increased hydrophicity (incorporation of long chain aliphatics and aryl groups), and reduction in overall cohesive energy and cross-link densities brought about by incorporation of substituted monofunctional cyanates provided good results in the copolymer series. The nonlinearity of moisture pick-up values with polymer compositions during water boil is probably associated with changes in diffusion rates and reflects the complexity of these interactions. The BPADC-F systems again demonstrate the lower water uptake of the fluorinated copolymer.

The fluorinated monomer cost was felt to be prohibitive but may be justified if the mechanical properties and fiber properties translation characteristics prove outstanding. The very low moisture absorptions experienced with this comonomer must be extended into composite form. The nominal Tg shift indicates that the elevated temperature strength reduction due to water sorption would be quite low. Further work with the dry and wet laminates was needed to establish this, but time and contract use limitations prevented an investigation.

Catalyst Screening

Cure temperatures of 424K (300°F) should give Tg's up to perhaps 444K (340°F). "Wet" Tg's can probably be tolerated to as low as 388K (240°F), recalling the severity of the water boil test. The BPADC/NPC system in the 80/20 to 70/30 region appeared to offer the best opportunity for attaining properties in an economical manner. These

systems also provided stable B-staged resins with suitable viscosities, depending on composition and "cook time" for facile hot melt prepreg preparations. The staged resins showed no signs of crystallizing after prolonged ambient temperature exposure.

To achieve a more reasonable cure schedule (shortened cure and postcure times), a brief study on potential catalyst systems for the BPADC/NPC materials was conducted. The uncatalyzed "cook times" referred to above generally were 4 to 5 hours at temperatures as high as 453K (356°F). At this point (~50 percent reaction), the time required for gelation at 394K (250°F) was in excess of two hours, much too long for a reasonable processing schedule.

The trimerization of cyanate groups is strongly subject to catalysis by a variety of materials. Lewis acids and bases, salts such as sodium acetate, sodium boronate and even lithium chloride, proton acids, bases and heavy metal organic salts have been found suitable. The rate of trimerization depends on the chemical nature of the polycyanate material and the temperature and purity of the monomers (absence of trace catalysts). Our studies dealt exclusively with metal-containing organic materials. Two main catalyst groups, metal stearates and metal acetylacetonates, were employed. To avoid the problems of multiple melting points in the DSC scans, the BPADC was B-staged to a viscous resin by heating several hours at 424K (300°F). The resin was mixed with the appropriate amount of catalyst and the DSC scan run. The results are listed in Table 3.

The stearates, notably zinc stearate, are usually quite effective in catalyzing the trimerization of BPADC. Interestingly, aluminum stearate appears to have no effect. The other stearates and acetylacetonates all lower the reaction exotherm temperature but are less efficient than the zinc salt. The stearates have the advantage of being soluble in the staged resin and the resulting polymers appear to be homogeneous. The acetylacetonates, on the other hand, are not particularly soluble in the resin and form local "hot spots" on polymerization. The stearates also have an added cost advantage over the acetylacetonates, costing roughly $1.00/lb compared to $100/lb for acetylacetonates.

Small samples of staged 80/20 BPADC/NPC resin were mixed with varying amounts of zinc stearate (0.2, 0.4, and 0.6 percent) and heated at 400K (261°F) until gelation occurred. Figure 5 is a plot of the gelation time versus concentration of catalyst at 400K (261°F). Carbon fibers, when mixed with the staged resin and catalyst, seem to slightly accelerate the gel time. Infrared studies show no difference in the slight residual cyanate absorbance at 2260 cm^{-1} relative to the aromatic region between the 0.4 and 0.6 percent loadings (postcured six hours at 422K (300°F). A catalyst loading of 0.5 percent gave a reasonable gel time at 394K (250°F).

Table 3. Catalyst Evaluations

Catalyst	Concentration (%)	Reaction Exotherm Maxima, Degrees K(F)
BPADC - Control	0.00	485 - 496 (413-433)
$Zn(St)_2$	0.45	474(394)
$Zn(St)_2$	0.62	470(387)
$Zn(St)_2$	1.39	468(383)
$Al(St)_3$	0.50	485(414)
$Al(St)_3$	1.43	484(412)
$Al(St)_3$	2.19	486(415)
$Pb(St)_2$	4.22	466(379)
$Fe(St)_2$	1.62	471(388)
$Ni(St)_2$	1.19	475(396)
Zn AcAc	1.14	473(392)
An AcAc	2.17	473(392)
Zn AcAc	2.94	466(379)
Ni AcAc	0.54	480(405)
Cu AcAc	2.60	471(388)
Fe AcAc	1.11	468(383)
Cr AcAc	1.49	453(356)

St = Stearate AcAc = Acetylacetonate

Prepreg Preparation

Standard drum winding procedures were employed in preparing the T-300/BPADC-NPC (80/20) prepreg. Using our laboratory equipment, three-foot lengths of six-inch wide prepreg with a 24 tows/inch fiber spacing were prepared. The underlying resin film was pulled to a 0.004 in. thickness between plastic sheets, the sandwiched resin then taped to the drum, the outer plastic stripped off and the tensioned fiber wound on. The fiber was thoroughly impregnated by warming the resin/fiber overwrap on a vacuum table at 344K (160°F) and squeegeeing while under the vacuum bag. The resulting prepreg had a resin content of 45-47 percent by weight and good uniformity.

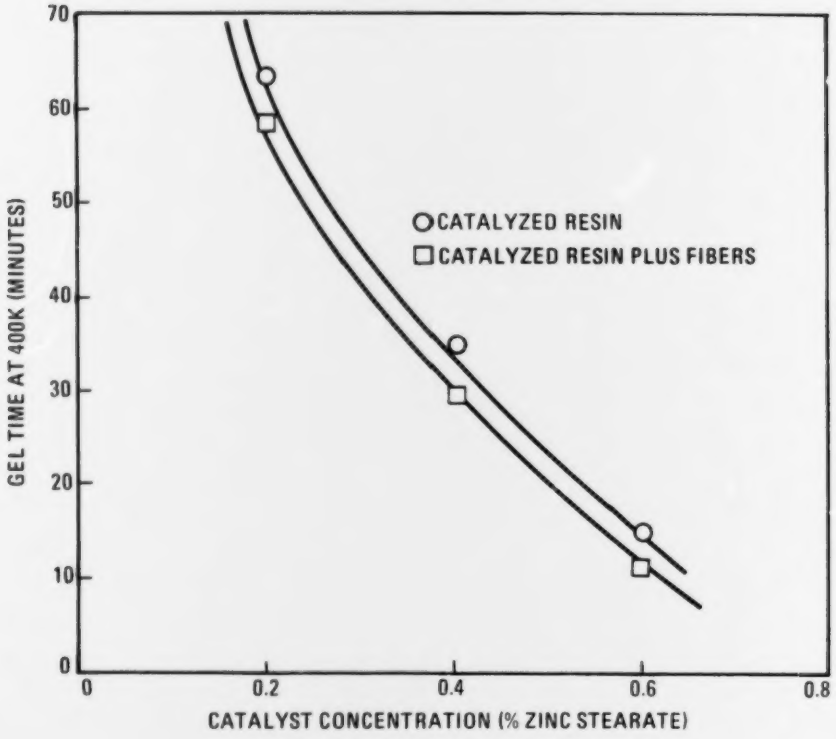


Figure 5. Gel Time of 80/20 BPADC/NPC at 400K (261°F)

Laminate Fabrication

A twelve ply unidirectional laminate was laid up according to Figure 6.

Cure was accomplished as follows:

a. Apply full vacuum and hold for 30 minutes.

b. Heat to 400K (261°F) at 2-3K per minute.

c. After 5 minutes, apply 14.5 MPa (100 psi) and hold 120 minutes.

d. Cool to room temperature, vent pressure, and carefully disassembly.

e. Postcure at 424K (300°F) for 4 hours starting from a cold oven.

After the laminate was wet-sawed into short beam shear and flex specimens, initial property values were determined. The remaining specimens were subjected to the two aging conditions described in the following section.

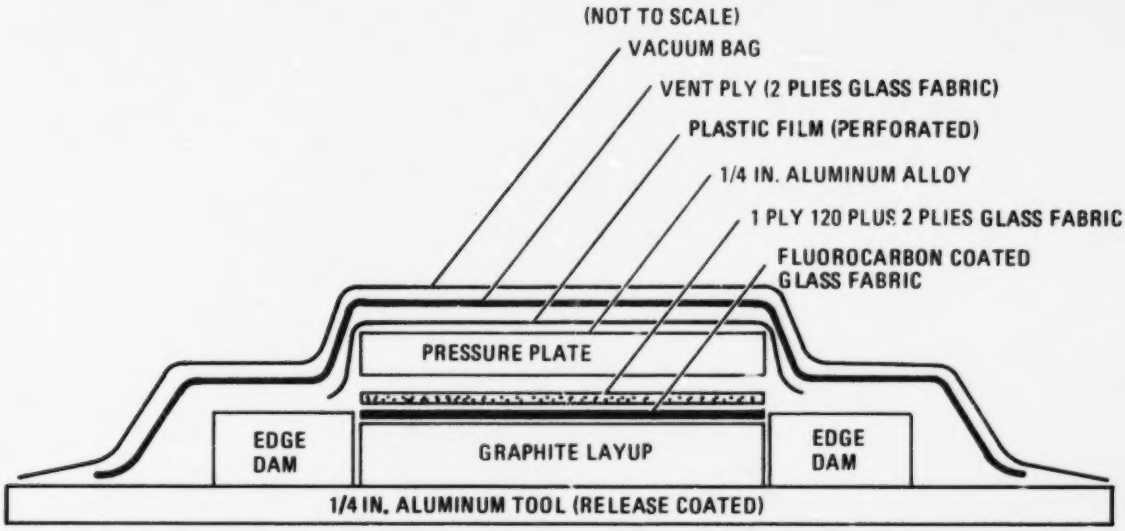


Figure 6. Layup Sequence

Aging Studies

Specimens were exposed to heat aging at 366K (200°F) for 500 hours in circulating air. Except for a very slight initial weight loss (<0.05%), which can be attributed to absorbed moisture, there was no change in specimen weights throughout the entire aging period.

Humid aging at 95 + percent relative humidity (RH) and 322K (120°F) for 500 hours resulted in a monimal weight gain of between 0.26% and 0.30% for short beam shear and flex specimens. The weight gains are presented in Figure 7 as a function of the square root to time. Fick's Diffusion Law predicts a linear plot. The roll-off, as equilibrium is approached, is quite commonly seen in composites.

Laminate Properties

Testing of the moisture laden samples was performed within an hour after removal from the humidity chamber. The elevated temperature test procedure was to load the sample in the test fixture, which was enclosed by a preheated oven, and initiate the test two minutes after the oven door was closed. Thermocoupled specimens showed that the test temperature was reached between 45 and 60 seconds after fixture loading. This procedure was followed to ensure minimal loss of sorbed moisture and at the same time approach the most severe conditions. Moisture loss during the test was never more than 7 percent of the total amount absorbed. The results are

presented in Table 4 along with the heat-aging and original laminate data. The retention values as a percentage of the original are included. All results are an average of three tightly grouped (<10 percent variation) specimens.

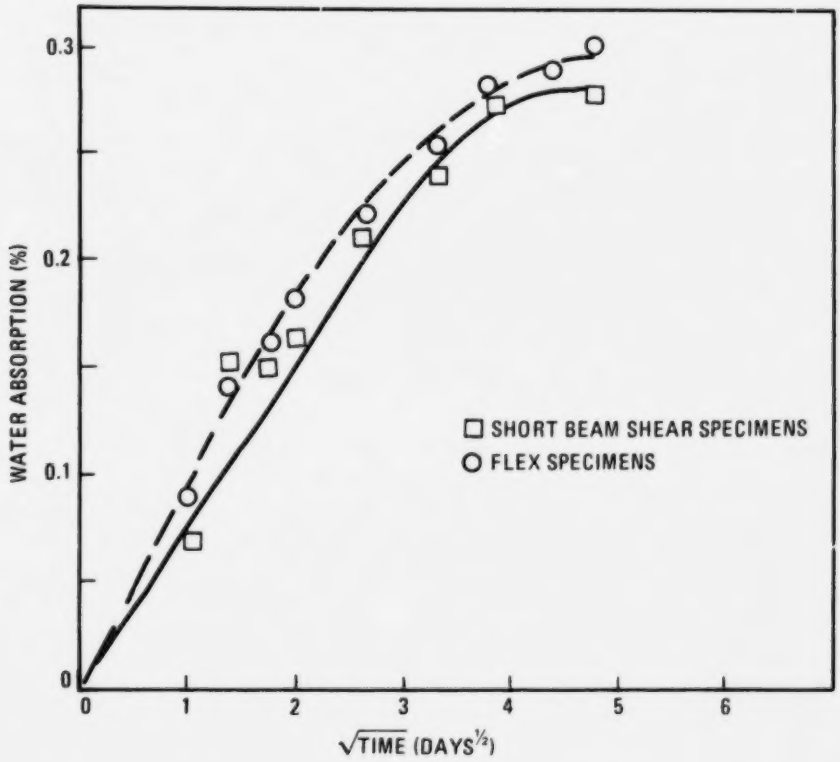


Figure 7. Water Absorption of 80/20 BPADC/NPC Laminate Specimens

CONCLUSIONS

The results displayed in Table 4 are very gratifying. The as-fabricated values are comparable to those attainable with any epoxy matrix in use. Room temperature and 355K (180°F) results reflect the characteristics expected from a matrix resin that efficiently translates fiber properties into composite performance. The retention of the room-temperature properties at elevated temperature is to be expected from such a resin at temperatures somewhat below its glass transition temperature. Heat aging at 366K (200°F) shows essentially no effect on composite performance. A most significant result is in the retention of the original properties after humid aging. Flexural properties are virtually unchanged, while the short beam shear strengths show a nominal decrease of between 15 and 30 percent. These results were obtained

Table 4. Unidirectional T-300[1]/BPADC-NPC (80/20 mole ratio) Laminate Data

Aging Conditions	Resin Volume, Percent	Fiber Content, Percent	Void Content, Percent	Short Beam Shear Strength,† MPa(kpsi) RT	Short Beam Shear Strength,† MPa(kpsi) 355K (180F)	Flexural Strength/Modulus MPA/GPa (kpsi/mpsi) RT	Flexural Strength/Modulus MPA/GPa (kpsi/mpsi) 355K (180F)
As Fabricated	27.9	63.8	1.6	88.9 (12.9)	72.3 (10.5)	1523/133(221/19.3)	1440/125(209/18.2)
Heat Aged*	-	-	-	88.9 (12.9)	53.7 (7.8)	1633/136(237/19.7)	1357/125(197/18.2)
Percent Retention				(100)	(74.3)	(107.2)	(94.2)
Humidity Aged**	-	-	-	75.8 (11.0)	51.7 (7.5)	1564/134(227/19.4)	1364/124(198/18.0)
Percent Retention				(85.3)	(71.5)	(102.7)	(94.7)

*500 hours at 366K (200F) -<0.1% weight loss

**500 hours at 322K (120F)/95 +% RH - SBS specimens showed 0.30% weight gain
- Flex specimens showed 0.26% weight gain (saturated)

† T300/5209 (Narmco)[1] yields the following results:

Test Temperature Deg K (F)	Condition	Short Beam Shear Strength MPa (kpsi)
RT	Dry	88.9 (12.9)
RT	Wet	75.1 (10.8)
324 (120)	Wet	61.3 (8.9)
344 (160)	Wet	48.2 (7.0)

[1] T-300 graphite fiber-Trademark of Union Carbide Corporation
5209 - Designation of proprietary epoxy formulation from Narmco Materials, Inc. A division of Celanese Corp.

with unoptimized processes (cf. the relatively high void content, 1.4 percent) from the prepreg and laminate fabrication standpoint. They can be expected to only improve with optimized prepreg preparation and processing technique refinements.

The objective of demonstrating the potential of cyanate resins as matrix resins for graphite fiber reinforced composites has certainly been met. The overall objective of developing a tougher, more moisture resistant laminating resin with cost, handleability, process requirements and mechanical properties equivalent to current high performance 400K (260°F) curing epoxy systems appears to be readily attainable. Application and expansion of the technique and benchmark data obtained during this feasibility study will facilitate such a program.

These preliminary results describe the inherent adaptability of cyanate resin chemistry available through monomer selection and formulation changes to accommodate a wide range of end-use requirements. Further development of these materials to provide an optimized system for current requirements and to expand their utility to a wider range of end-use applications is recommended.

EXPERIMENTAL

The following description exemplifies the general procedure followed for preparation of the cyanate monomers. Appropriate changes in amounts of reactants were made to maintain proper stoichiometry. Purification procedures included recrystallization for solids and fractional distillation (15 cm helix-packed, vacuum-jacketed column) for the liquid p-nonylphenyl cyanate. Yield and recrystallizing solvent data are shown in Figure 8.

PREPARATION OF CYANATE ESTERS

A three-necked 1000 ml round bottomed flask was equipped with a mechanical stirrer, thermometer and an additional funnel. A slow stream of nitrogen swept through the apparatus, terminating in a sodium hydroxide/water/isopropanol solution gas trap. A solution of 65 g (1.05 moles) of cyanogen chloride in 300 ml of anhydrous acetone was prepared in the reaction flask and maintained at 263K (14°F). A solution of the appropriate phenol (1.0 mole hydroxy group) in 250 ml of anhydrous acetone was also added to the reaction flask. The solution was stirred and 101g (1.0 mole) of triethylamine slowly added maintaining the reaction mixture temperature below 273K (32°F). The solution was stirred an additional 30 minutes upon completion of the triethylamine addition. The reaction slurry was poured into three liters of stirred water and the crude product was separated. Solid products were air dried after a thorough water washing and recrystallized from the listed solvents. Liquid product was thoroughly washed, dried over sodium sulfate, filtered and then distilled.

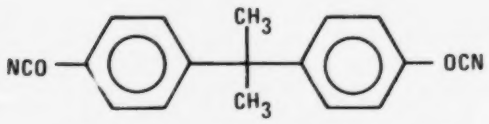
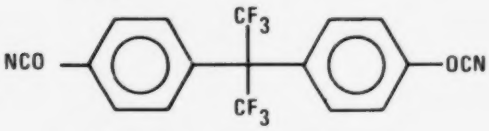
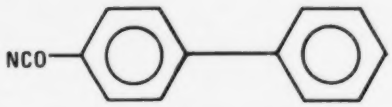
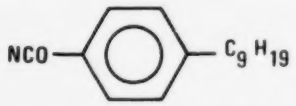
COMPOUND	PURIFIED YIELD	SOLVENT
 2,2-BIS (P-CYANATOPHENYL) PROPANE BPADC	86 PERCENT	PETROLEUM ETHER
 2,2-BIS (P-CYANATOPHENYL) HEXAFLUOROPROPANE BPADC-F	52 PERCENT	CYCLOHEXANE/LIGROINE (TWICE)
 4-PHENYLPHENYLCYANATE PPC	48 PERCENT	LIGROINE
 4-NONYLPHENYLCYANATE NPC	53 PERCENT	DISTILLED

Figure 8. Yield and Recrystallizing Solvent Data

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1. C. B. Delano and E. S. Harrison, Processable Laminating Resins With Improved Moisture Resistance, Toughness and Moderate Temperature Capability, Technical Report AFML-TR-73-216[1] Part I and II, December 1973 and March 1974.

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16. Abstract

The objective of the program was to demonstrate the feasibility of using cyanate resins as laminating systems with projected cost, handleability, and processing requirements equivalent to 400K (260°F) curing epoxies and to provide laminated structure of equivalent quality but with improved moisture resistance and toughness. Cyanate resins were found to be well suited for these applications. The program preceded from monomer synthesis, through formulation, blending, resin preparation, catalysis studies, prepreg preparation to laminate fabrication and test. The goal of the contract was met with fabrication of a graphite fiber reinforced laminate with 95 percent retention of the original 363K (180°F) flexural strength and 70 percent retention of the 363K (180°F) short beam shear strength after 500 hour exposure to 95+ percent relative humidity at 324K (120°F).

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